PICTURES OF MOLECULAR ORBITALS*

by

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I. Introduction

Motivated by a desire to bridge and if possible to stem the widening gap between the "computors" and the "non-computors" in molecular quantum mechanics as so disturbingly defined by C. A. Coulson (1960), this paper and others to follow presents directly and on a consistent basis pictorial representations of well defined quantum mechanical concepts. Here accurate charge density pictures of molecular orbitals ((MO's) very close to the Hartree-Fock MO's (Wahl 1966a) are given.

Recently much has been written elsewhere about the development and present state of the molecular orbital method (Lowdin and Pullman 1964, Slater 1965, Nesbet 1965) therefore, we shall confine ourselves to a brief statement of crucial steps in its history.

The molecular orbital method as introduced by Mulliken (1928-32) and Hund (1927) was used extensively in the semiempirical interpretation of band spectra, however, mathematically and computationally the concept matured rather slowly. Its early development (and the search for the "best" MO's) may be traced from the recognition by Lennard-Jones (1929) of its relationship to Hartrees self-consistent field work on atoms (1928), followed by the introduction of the determinantal form for the wave function (Slater 1930a, 1932) with the application of the variational principle (Fock 1930 ; Slater 1929, 1930b) to yield the now familiar pseudo-eigenvalue equations of the form

$$F\varphi_i = \epsilon_i \varphi_i \qquad (1)$$

known as the Hartree-Fock equations, which provide a rigorous mathematical definition of best orbitals. Lennard-Jones (1929) presented the equations

for an arbitrary system; Coulson (1938) foreshadowed their solution by the expansion method; and Roothaan (1951, 1960) developed and perfected the extensively used matrix formulation of the expansion method. Important also are the proofs by Delbruch (1939), Lowdin (1962), and Roothaan (1951) that the Hartree-Fock functions are always self-consistent, symmetry adapted and correspond to a specific minimum of the total energy. Extremely relevant to the potency and appeal of Hartree-Fock wave functions was the work of Brillouin (1933-4), Moller and Plesset (1934) on corrections to the Hartree-Fock approximation. They showed that one-electron properties computed from Hartree-Fock wave functions have first-order corrections in perturbation theory which vanish provided that degeneracy are not present. Koopman (1933) developed similar theorems for ionization potentials.

II. Hartree-Fock Molecular Orbitals as Linear Combinations of Expansion Functions

Having clearly defined the Hartree-Fock model of a molecular system it still remained a formidable practical problem to obtain the MO's Φ_i. In 1951 Roothaan had cast the Hartree-Fock equations into a solid computational framework remarkably suitable for the then embryonic digital computers. In what is now referred to as the Roothaan Method (1951, 1960) the orbital Φ_i is expanded in terms of some suitable truncated basis set χ_p

$$\Phi_i = \sum_p C_{ip} \chi_p \qquad (2)$$

The expansion coefficients C_{ip} are optimized through the iterative self-consistent field process (Roothaan and Bagus 1964). In the full numerology of the process the best truncated set of basis functions χ_p are also

hunted down, usually by brute force methods. In practice a very close approximation to the molecular orbitals can be obtained in this way. Calculations of this type utilizing analysis and computer programs developed recently (Wahl 1964), (Wahl et al 1964) have resulted in the determination of the molecular orbitals for a large number of diatomic molecules in the form of Eq. 2. These functions in which the basis set χ_p consists of many Slater type orbitals (STO's) are very close to the Hartree-Fock result. They were used in the pictorial calculations presented in this work (see "wave functions" in references).

III. Densities and Contours

At this point in order to clarify the diagrams of the shell model it is convenient to introduce two new indices λ and α which indicate respectively the symmetry species and subspecies of the molecular orbitals ϕ_i. The electronic density $\rho_{i\lambda}$ associated with the $i\lambda^{th}$ molecular shell at a point $\underset{\sim}{r}$ in space is defined by

$$\rho_{i\lambda}(\underset{\sim}{r}) = e^{-}N_{i\lambda}\, d_\lambda^{-1} \sum_{\alpha} \phi_{i\lambda\alpha}(\underset{\sim}{r})\, \phi^*_{i\lambda\alpha}(\underset{\sim}{r}) \qquad (3)$$

where we have now grouped the molecular orbitals $\phi_{i\lambda\alpha}$ according to their symmetry species λ and their subspecies α and have defined the density of shell $i\lambda$ which contains $N_{i\lambda}$ electrons in terms of the sum over the modulus squared of the d_λ degenerate molecular orbitals making up the shell. The total electron density $\rho(\underset{\sim}{r})$ of the molecule is then given by

$$\rho(\underset{\sim}{r}) = \sum_{\lambda} \sum_{i} \rho_{i\lambda}(\underset{\sim}{r}) \qquad (4)$$

and is thus the sum of the densities of all shells making up the molecule.

The density associated with one of the d_λ degenerate molecular orbitals $\phi_{i\lambda\alpha}$ making up shell $i\lambda$ is

$$\rho_{i\lambda\alpha}(\underset{\sim}{r}) = \rho_{i\lambda}(\underset{\sim}{r})/d_\lambda \qquad (5)$$

which is just the shell density divided by the number of degenerate molecular orbitals making up the shell. In the diagrams presented in this paper it is the total density (Eq. 4) and the orbital density (Eq. 5) which has been plotted. (For σ symmetry $d_\lambda = 1$ and thus the orbital density equals the shell density, for π symmetry in diatomic molecules $d_\lambda = 2$ and the orbital density equals 1/2 of the shell density. The molecular shells and their occupation $N_{i\lambda}$ are given in Table I for the molecules studied. The only molecular symmetries occurring in this work are σ_g, σ_u, π_u, and π_g.)

In what follows in this section the symmetry indices λ and α of the orbital density $\rho_{i\lambda\alpha}(\underset{\sim}{r})$ will be suppressed since they are unnecessary for the description of the contour drawing process.

An orbital contour line indicating a density C in the xz (ρ and ρ_i for diatomic molecules are cylindrically symmetric about the z axis and plots in any plane containing this axis convey complete density information) plane may be defined by the equation,

$$\rho_i(x,z) - C$$

and its path by the relation,

$$\frac{d\rho_i}{dx}\Delta x + \frac{d\rho_i}{dz}\Delta z = 0$$

which gives the direction of the tangent to the contour at any point on it to be:

$$\frac{\Delta x}{\Delta z} = -\frac{d\rho_i/dz}{d\rho_i/dx} \quad . \tag{6}$$

A step $\Delta s = (\Delta x^2 + \Delta z^2)^{\frac{1}{2}}$ is taken along this tangent and a density found such that

$$\rho_i\,'(x + \Delta x,\ z + \Delta z) = C + \Delta\rho_i \tag{7}$$

then a correction is applied perpendicular to initial tangent along the new line

$$\frac{\Delta x'}{\Delta z'} = +\frac{d\rho_i/dx}{d\rho_i/dz}$$

a distance

$$\Delta z' = \frac{\Delta\rho_i}{\frac{d\rho_i'}{dz'} + \frac{d\rho_i'}{dx'}\frac{d\rho_i/dx}{d\rho_i/dz}} \tag{8}$$

This correction (Eq. 8) is continued until $\Delta\rho_i$ falls within a small preset threshold. This hunt process (Eqs. 6-8) is continued until entire contour is traced out. Analogous equations result for the total molecular density or for any linear combination of molecular orbital densities.

The input to the computer program consists of the symmetry basis functions $\chi_{p\lambda\alpha}$ the orbital coefficients C_{ip} , the internuclear distance, a series of the contour values desired with the associated thresholds, and finally the physical scale in which diagrams are to be plotted. The output consisted of 35 mm negatives of the diagrams presented in this work. The process has been more completely documented elsewhere (Wahl 1966a).

IV. Results and Implications

In Table 3 the contours of density associated with the homonuclear diatomic molecules constructed from first row atoms are given on a consistent basis as defined in the key. (Table 2) Both the total molecular densities and the orbital densities are displayed. (These diagrams are available at a larger scale Wahl 1966a). It is hoped that in addition to their obvious tutorial value these contour diagrams of the molecular orbital model for these simple homonuclear diatomic molecules, H_2, Li_2, B_2, C_2, N_2, O_2, and F_2 will prove to be useful symbols which will stimulate thought about chemical binding, steric hindrance, bonding and antibonding orbitals in addition to providing a correct and more complete picture of molecular orbitals where only a rudimentary one, based primarily on hydrogen atom wave functions and single STO's, existed before.

Using these computational techniques, concepts and changes which are best presented visually may be so presented. Such visual presentations have been quite limited in the past due to the prohibitive labor involved (Huo 1965) (Peyerimhoff 1965). Studies of interatomic forces and the formation of the chemical bond using extended Hartree-Fock wave functions (Das and Wahl 1966) are underway in which these programs are being used to display the changes occurring in electronic charge density as a

molecule forms. In a study of molecular ionization these automatic contour programs are being used to illustrate directly changes in the molecular charge distribution with electron removal. In other theoretical work a pictorial display of configuration mixing provides a physical picture of wave function improvements and electron correlation as produced by added optimal configurations. This work contains the development of a new tool; namely, the synthesis of high speed digital computers and linked analog devices into a medium capable of efficiently communicating certain types of new information. Since many of us involved in large scale computational efforts are often swamped by our own computer output and are able to competently analyze only a small fraction of the potentially useful information we have generated this problem of communication well worth consideration (Coulson 1960).

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It is indeed a pleasure to contribute this work to a volume honoring Professor J. C. Slater. In the long analytic and computational path which finally lead to these pictures, his concepts have been always at hand,

namely; the Slater type orbitals which formed the basis sets, the Slater determinantal form of the wave function, and in addition his early contributions to Hartree-Fock theory itself as well as his many and substantial educational contributions (Slater 1963).

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Wavefunctions: The molecular orbital SCF wave function used--- F_2 (Wahl 1964); O_2 (Malli, G. L. and Cade, P. E. to be published); N_2 (Wahl et al 1966b); C_2 and B_2 (Greenshields, J. to be published; Li_2 (Sales, K. D., Cade, P. E., Wahl, A. C. to be published); H_2 (Das and Wahl 1966). All wave functions are comparable in sophistication to the published F_2 and N_2 functions. The basis sets have been extensively optimized and explored. All these MO wave functions can be obtained on request from the author or from C. C. J. Roothaan and P. E. Cade at the Laboratory of Molecular Structure and Spectra, Chicago.